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⑯ **Hydroxylation of olefins.**

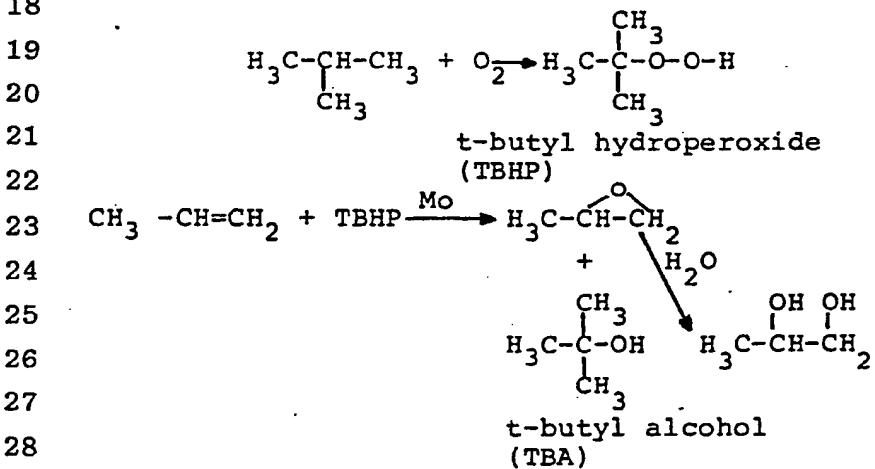
⑯ A process for the hydroxylation of olefins comprises
reacting the olefin with an oxygen containing gas and water
in the presence of a defined catalyst composition. The cat-
alyst composition comprises (i) a catalytically active oxide
of a specified metal such as OsO₄, (ii) a co-catalyst I being
a specified transition metal salt such as CuBr₂, and (iii)
optionally a co-catalyst II being a salt such as tetra ethyl
ammonium bromide.

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HYDROXYLATION OF OLEFINS

1 The present invention relates to a process for
2 converting olefinically unsaturated compounds to their
3 corresponding diols or polyols in the presence of a
4 specifically defined oxidation catalyst composition,
5 water, and an oxygen containing gas.

6 Processes for the production of glycols, such
7 as ethylene glycol, from olefins are well known in the
8 art. One class of these processes involves the conver-
9 sion of an olefin, e.g., ethylene, to its corresponding
10 oxide, e.g., ethylene oxide, as an intermediate. This
11 intermediate is subsequently hydrolyzed to form the cor-
12 responding glycol. Prominent in this class of processes
13 is a method wherein an olefinic compound is reacted with
14 an organic hydroperoxide compound in the presence of a
15 molybdenum catalyst to form the corresponding oxide.
16 The organic hydroperoxide preferably is formed by react-
17 ing an aliphatic saturated compound with oxygen. The
 reaction scheme can be summarized as follows:



29 The commercial attractiveness of this process is dependent
30 on the ability to use or sell the organic alcohol
31 co-product. Given the fluctuation in economic condi-
32 tions, however, it may be difficult to dispose of large
33 quantities of these organic alcohol co-products in an

1 economically attractive manner. In any event, it can
2 be troublesome, when the quantity of one product, se-
3 lected on the basis of marketing possibilities for a
4 given period, necessarily determines the quantity of
5 some other product which may be smaller or larger than
6 desirable in view of changing marketing requirements
7 within that same period. It can, therefore, under cer-
8 tain circumstances be considered as a disadvantage of
9 the aforesaid process that such large quantities of or-
10 ganic alcohols are formed as co-products, even though
11 under other circumstances the formation of two products
12 may well be found acceptable.

13 An alternative multi-stage method for making
14 ethylene glycol involves the oxidation of ethylene to
15 ethylene oxide at elevated temperatures and pressure us-
16 ing oxygen and a silver containing catalyst. The ethy-
17 lene oxide is then hydrated either catalytically using
18 a diluted aqueous solution of a strong acid, or at high
19 temperatures and pressures, with some diethylene and
20 triethylene glycols being formed as by-products. Be-
21 cause, in the first reaction stage (i.e., ethylene to
22 ethylene oxide) one molecule of oxygen theoretically
23 forms one molecule of carbon dioxide from the ethylene,
24 the maximum theoretical selectivity of this reaction is
25 at best 85%. Moreover, the first stage of reaction re-
26 quires very careful control of the operating conditions
27 just to obtain selectivities in the range of 60 to 70%.
28 Thus, rigid process control and by-product formation are
29 disadvantages of this type of indirect glycol formation.

30 An alternative approach to glycol formation in-
31 volves the catalytic oxidation of olefins directly to
32 form the corresponding glycol without the formation of
33 olefin oxide intermediates.

34 For example, it is well known from the techni-
35 cal literature and patents that olefins can be effective-
36 ly directly oxidized with a strong oxidizing agent in the
37 presence of catalytic amounts of osmium oxides, e.g.,

1 osmium tetroxide, e.g., to their corresponding
2 glycols.

3 More specifically, Japanese Patent applica-
4 tion No. Sho 54-145604, published November 14, 1979,
5 is directed to a process for hydroxylating olefins in
6 the presence of OsO_4 , a quaternary ammonium salt such
7 as tetra ethyl ammonium bromide, and a peroxide in-
8 cluding organo peroxides and H_2O_2 as the oxidant. The
9 use of oxygen as the oxidant is not disclosed nor is
10 the co-presence of co-catalyst I salts as described
11 herein disclosed. Selectivities to glycol of from about
12 4.5 to about 66% are disclosed. H_2O_2 oxidant in com-
13 bination with OsO_4 is known as Milas reagent which can
14 lead to non-selective oxidation of olefins as well as
15 over oxidation. H_2O_2 is also substantially more expen-
16 sive than oxygen or air. Accordingly, the uses of
17 organohydroperoxides as well as H_2O_2 as oxidants are
18 each associated with their own disadvantages.

19 U.S. Patent No. 2,414,385 discloses the use of
20 hydrogen peroxide and a catalytically active oxide, such
21 as osmium tetroxide, dissolved in an essentially anhy-
22 drous, non-alkaline, inert, preferably organic, solvent,
23 to convert, by oxidation, unsaturated organic compounds
24 to useful oxygenated products such as glycols, phenols,
25 aldehydes, ketones, quinones and organic acids. The
26 formation of glycols is achieved by conducting the reac-
27 tion at temperatures of between several degrees below
28 $0^{\circ}C$ and $21^{\circ}C$. Such low reaction temperatures drastically
29 and disadvantageously, reduce the reaction rate to com-
30 mercially unacceptable levels. At temperatures greater
31 than $21^{\circ}C$, the formation of aldehydes, ketones, and
32 acids is favored.

33 U.S. Patent No. 2,773,101 discloses a method
34 for recovering an osmium containing catalyst such as
35 osmium tetroxide, by converting it to the non-volatile
36 osmium dioxide form, distilling the hydroxylation product,
37 re-oxidizing the osmium dioxide to the volatile osmium

1 tetroxide, and then recovering the same by distilla-
2 tion. Suitable oxidizing agents used to oxidize ole-
3 fins, and re-oxidize the osmium dioxide, include in-
4 organic peroxides such as hydrogen peroxide, sodium
5 peroxide, barium peroxide; organic peroxides, such as
6 t-butyl peroxide or hydroperoxide, benzoyl peroxide;
7 as well as other well known oxidizing agents such as
8 oxygen, perchlorates, nitric acid, chlorine water and
9 the like. As with other methods of the prior art, the
10 above process yields undesirable by-products (see col.
11 1 line 55) thus reducing the selectivity of the process.

12 British Patent Specification No. 1,028,940 is
13 directed to a process for regenerating osmium tetroxide
14 from reduced osmium tetroxide by treatment of the latter
15 with molecular oxygen in an aqueous alkaline solution.
16 More specifically, it is disclosed that when osmium
17 tetroxide is used by itself as an oxidizing agent, or
18 as a catalyst in conjunction with other oxidizing agents,
19 to oxidize hydrocarbons the osmium tetroxide becomes
20 reduced, and in its reduced form is less active than
21 osmium tetroxide itself. Consequently, by conducting
22 the oxidation reaction in the presence of an alkaline
23 medium and supplying oxygen to the medium throughout the
24 process, the osmium tetroxide is maintained in a high
25 state of activity. The oxidation products disclosed in-
26 clude not only ethylene glycol from ethylene but also
27 organic acids from such compounds as vicinal glycols,
28 olefins, ketones, and alcohols. While the pH of the
29 alkaline medium is disclosed broadly for all possible
30 reactions as varying from 7.5 to 12 for purposes of re-
31 oxidizing reduced osmium tetroxide, the pH employed in
32 the example for preparing ethylene glycol is 9.5. If
33 the pH is too high, a wide variety of products is pro-
34 duced as a result of over oxidation and/or degradation.
35 Thus, the sensitivity of the process to the pH of the
36 medium necessitates rigid pH control which is economi-
37 cally disadvantageous.

1 U.S. Patent No. 4,255,596 is directed to a
2 process for preparing ethylene glycol in a homogeneous
3 single-phase reaction medium using ethylbenzene hydro-
4 peroxide as the oxidizing agent dissolved in ethylben-
5 zene and osmium tetroxide as the catalyst. The pH of
6 the reaction medium is maintained at about 14 by the
7 presence of tetraalkyl ammonium hydroxide. A small
8 amount of water can dissolve beneficially in the medium
9 to reduce by-product formation and improve selectivity
10 to the glycol.

11 U.S. Patent No. 4,049,724 describes the prepar-
12 ation of glycols from alkenes and from unsaturated
13 alcohols in an aqueous system using osmium tetroxide
14 and specifying stable and water-soluble aliphatic hydro-
15 peroxides, such as tert-butyl hydroperoxide, while a
16 critical pH of 8 to 12 is maintained by a suitable com-
17 bination of alkali metal buffering compounds. The prep-
18 aration of propylene glycol utilizing tert-butyl hydro-
19 peroxide is exemplified in the patent at a selectivity
20 based on the hydroperoxide of 45 percent.

21 None of the aforesaid patents disclose the
22 osmium containing-co-catalyst system described herein.

23 See also: U.S. Patent No. 3,317,592 (produc-
24 tion of acids and glycols using oxygen as oxidant, OsO_4
25 as catalyst at pH 8-10); U.S. Patent No. 3,488,394 (dis-
26 closes hydroxylation of olefins by reacting olefin and
27 hypochlorite in the presence of OsO_4); U.S. Patent No.
28 3,486,478 (discloses reaction of hypochlorite and ole-
29 fin in an aqueous medium and in the presence of OsO_4
30 catalyst to hydroxylate the olefin); U.S. Patent No.
31 3,928,473 (hydroxylation of olefins to glycols with O_2
32 oxidant, octavalent osmium catalyst (e.g., OsO_4), and
33 borates as promoter); U.S. Patent No. 3,931,342 (dis-
34 closes a process for recovering glycols from an
35 aqueous solution containing alkali metal borate and
36 osmium compounds [e.g., OsO_4]); U.S. Patent No. 3,953,305
37 (discloses use of OsO_4 catalyst for hydroxylating olefins

1 which is regenerated by oxidizing hexavalent osmium with
2 hexavalent chromium and electrochemically regenerating
3 hexavalent chromium); U.S. Patent No. 4,203,926 (dis-
4 closes ethylbenzene hydroperoxide as oxidant used in two
5 phase system to hydroxylate olefins in presence of OsO_4
6 and cesium, rubidium and potassium hydroxides); U.S.
7 Patent No. 4,217,291 (discloses the oxidation of Osmium
8 (III) or (IV) in an ionic complex with oxygen and an
9 alkali metal, ammonium, or tetra (-lower) alkyl ammonium
10 cation to a valency of greater than +5 + organo hydro-
11 peroxides); and U.S. Patent No. 4,229,601 (discloses the
12 use of cesium, rubidium and potassium hydroxides as pro-
13 moters for OsO_4 catalyst and t-butyl hydroperoxide oxi-
14 dant for hydroxylating olefins).

15 None of the aforesaid patents discloses the
16 catalytically active metal oxide-co-catalyst I system
17 described herein either alone or in combination with at
18 least one co-catalyst II described herein.

19 According to the present invention, there
20 is provided a process for hydroxylating at
21 least one olefinic compound having at least one ethylenic
22 unsaturation which comprises reacting said olefinic com-
23 pound with oxygen and water in the presence of a catalyst
24 composition in a manner and under conditions sufficient
25 to convert at least one of said ethylenic unsaturation to
26 its corresponding diol, said catalyst composition compris-
ing:

27 (a) at least one catalytically active metal ox-
28 ide wherein the metal of said oxide is selected from the
29 group consisting of Os, Ti, Zr, Nb, Cr, Mo, W, Ru, Re,
30 and Ir;

31 (b) at least one co-catalyst I transition metal
32 salt having a cation and an anion wherein said cation is
33 of a transition metal independently selected from the
34 group consisting of Fe, Co, Ni, Cu, V, Cr, Mn, Sc, Ti,
35 Mo, Ru, Rh, Pd, and W; and said anion is of a member

1 independently selected from the group consisting of hal-
2 ide, carboxylate, aryloate, aryolate, psuedo halide,
3 R_5S^- , HS^- , R_5Se^- , HSe^- , HTe^- , and R_5Te^- , R_5 being alkyl
4 of from about 1 to about 10 carbons; and

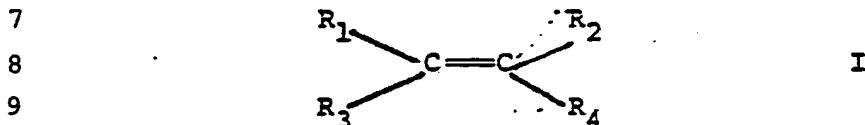
5 (c) optionally at least one co-catalyst II hav-
6 ing a cation and an anion wherein said cation is of
7 a member independently selected from the group consist-
8 ing of alkali metal, alkaline earth metal, tetra hydro-
9 carbyl ammonium, and tetra hydrocarbyl phosphonium, said
10 hydrocarbyl group being selected from the group consist-
11 ing of substituted and unsubstituted alkyl, aryl, alkaryl
12 and aralkyl, and said anion is of a member independently
13 selected from the group consisting of halide, carboxyl-
14 ate, aryloate, aryolate, psuedo halide, hydroxyl, R_5S^- ,
15 HS^- , R_5Se^- , HSe^- , HTe^- , and R_5Te^- said R_5 being alkyl
16 as defined above.

17 Thus, in summary, at
18 least one olefin containing at least one ethylenic un-
19 saturation is reacted with oxygen and water in the pres-
20 ence of a catalyst composition comprising a catalytically
21 active metal oxide, at least one co-catalyst I as described
22 herein, and optionally at least one co-catalyst II as
23 described herein to convert at least one of said ethyl-
24 enic unsaturation to its corresponding diol.

25 Olefins which can be hydroxylated in accordance
26 with the present invention contain at least one ethylenic
27 unsaturation and comprise any of the unsaturated ali-
28 phatic or alicyclic compounds well known in the art for
29 undergoing such hydroxylation reactions. Typically,
30 such compounds will contain from about 2 to about 20 car-
31 bons, preferably from about 2 to about 10 carbons, and
32 most preferably from about 2 to about 5 carbons. Such
33 compounds may be straight or branched chain, mono-olefinic,
34 di-olefinic, or polyolefinic, conjugated or non-conju-
35 gated. They may be substituted with such groups as aryl,
preferably aryl of from 6 to about 14 carbons, alkyl,

1 preferably alkyl of from 1 to 10 carbons, or aralkyl and
 2 alkaryl wherein the alkyl and aryl portions thereof are
 3 as described above, as well as with functional groups
 4 such as hydroxyl, carboxyl and anhydride.

5 Typical of such olefins are those represented
 6 by the structural formula:



10 wherein R₁, R₂, R₃, and R₄, which may be the same or
 11 different, are selected from the group consisting of
 12 hydrogen; substituted or unsubstituted: alkyl, aryl,
 13 alkaryl, and aralkyl hydrocarbyl groups, said hydrocar-
 14 byl groups being preferably as defined immediately above;
 15 or any two of said R₁₋₄ groups together can constitute
 16 a cycloalkyl group typically of from about 4 to about
 17 12, preferably from about 5 to about 8 carbons.

18 Representative olefins which can be hydroxylated
 19 and contain at least one ethylenic unsaturation include: ethylene,
 20 propylene, butene-1, butene-2, isobutene, pentene-1, pentene-2
 21 hexene, isohexene, heptene, 3-methylhexene, octene-1,
 22 isooctene, nonene, decene, dodecene, tridecene, pentade-
 23 cene, octadecene, eicosene, docosene, tricosene, tetra-
 24 cosene, pentacosene, butadiene, pentadiene, hexadiene,
 25 octadiene, decadiene, tridecadiene, eicosadiene, tetra-
 26 cosadiene, cyclopentene, cyclohexene, cycloheptene,
 27 methylcyclohexene, isopropylcyclohexene, butylcyclohexene,
 28 octylcyclohexene, dodecyclohexene, acrolein, acrylic
 29 acid, 1, 2, 3, 4-tetra-hydrophthalic anhydride, methyl
 30 methacrylate, styrene, cholesterol, and the like.

31 The preferred olefins are ethylene, propylene,
 32 isobutylene, styrene, allyl alcohol and allyl chloride.

33 The most preferred olefins are propylene and ethylene.

34 The catalytically active metal oxide includes
 35 oxides, well known in the art as oxidation catalysts, such
 36 as transition metal oxides including those of Os, Ti, Zr,

1 V, Nb, Cr, Mo, W, Ru, Re, and Ir.

2 Representative catalytically active metal oxides
3 include: OsO₂, OsO₄, TiO₂, ZrO₂, Nb₂O₃, V₂O₅, CrO₃,
4 MoO₃, WO₃, Re₂O₇, IrO₂, and the like.

5 The preferred catalytically active metal oxide
6 is osmium tetroxide.

7 Co-catalyst I is a term used to refer to at
8 least one organic or inorganic transition metal salt hav-
9 ing an anion and a cation, wherein the anion of said salt
10 includes halide, pseudo halide, carboxylate, aryloate,
11 and aryolate and other anions described hereinafter.

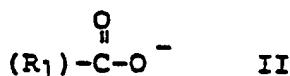
12 More specifically, the cation transition metals
13 of said co-catalyst I salts include those with a variable
14 oxidation state such as Fe, Co, Ni, Cu, V, Cr, Mn, Sc,
15 Ti, Mo, Ru, Rh, Pd, and W.

16 The preferred transition metal cations include
17 those of Cu, Fe, Ni, Co, and Mn, most preferably Cu.

18 More specifically, the anion of co-catalyst I
19 includes:

20 (a) halide ions such as fluoride, chloride,
21 bromide, and iodide, preferably chloride, bromide, and
22 iodide;

23 (b) carboxylate anions, typically carboxylate
24 anions represented by the structural formula:



25 wherein R₁ is selected from the group consisting of substi-
26 tuted and unsubstituted: alkyl, typically about C₁ to about
27 C₁₀ alkyl, preferably about C₁ to about C₅ alkyl, and most
28 preferably about C₁ to about C₃ alkyl, and aralkyl, typi-
29 cally aralkyl wherein the aryl group thereof is as defined
30 in connection with Ar of structural formula III below and
31 the alkyl group thereof is as defined immediately above;
32 said R₁ substituents including hydroxyl; halide (i.e.,
33 F, Cl, Br, and I); ether groups, typically ether groups
34 represented by the structural formulae -O-R₂, and
35 -R₃-O-R₂ where R₂ and R₃ are independently selected from

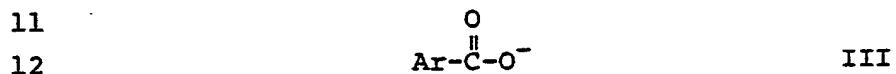
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1 the group consisting of alkyl, typically about C₁ to
 2 about C₁₀ alkyl, preferably about C₁ to about C₅ alkyl
 3 and most preferably about C₁ to about C₃ alkyl; and ester
 4 groups, typically ester groups, represented by the

5 structural formulae $\begin{matrix} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{R}_4 \end{matrix}$, $\begin{matrix} \text{O} \\ \parallel \\ -\text{O}-\text{C}-\text{R}_4 \end{matrix}$, $\begin{matrix} \text{O} \\ \parallel \\ -\text{R}_5-\text{O}-\text{C}-\text{R}_4 \end{matrix}$, and

6 $\begin{matrix} \text{O} \\ \parallel \\ \text{R}_5-\text{O}-\text{C}-\text{R}_4 \end{matrix}$, wherein R₄ and R₅ which may be the same or
 7 different are as defined in connection with R₂ and R₃;

8 (c) aryloate anions, typically aryloate anions
 9 represented by the structural formula:



12 wherein Ar is selected from the group consisting of sub-
 13 stituted and unsubstituted: aryl, typically C₆ to about
 14 C₁₄ aryl, preferably C₆ to about C₁₀ aryl (e.g., C₆ aryl)
 15 and alkaryl, typically alkaryl wherein the alkyl group is
 16 as defined above in connection with R₁ being alkyl, and
 17 the aryl group thereof is as defined above, and wherein
 18 said substituents on the Ar group are as defined above
 19 in connection with R₁;

20 (d) aryolate anions, typically aryolate anions
 21 represented by the structural formula:



23 wherein Ar is as described above in connection with
 24 structural formula III, and preferably is aryl; and

25 (e) pseudo halide anions, defined herein to
 26 be selected from the group consisting of SCN⁻, CN⁻,
 27 SeCN⁻, TeCN⁻, OCN⁻, and CNO⁻; and

28 (f) anions selected from the group consisting
 29 of R₅S⁻, HS⁻, R₅Se⁻, HSe⁻, HTe⁻, and R₅Te⁻, R₅ being
 30 alkyl typically about C₁ to about C₁₀ alkyl, preferably
 31 C₁ to C₅ alkyl.

32 In short, the co-catalyst I salt can be a single
 33 salt, or a mixture of salts and said salts can comprise
 34 any of the aforesaid transition metal cations associated
 35 with any of the aforesaid group (a)-(f) anions.

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1 Representative examples of co-catalyst I salts
2 include FeF_3 , FeCl_3 , FeBr_3 , FeF_2 , FeCl_2 , FeBr_2 , FeI_2 ,
3 CoCl_2 , CoF_3 , CoF_2 , NiF_2 , NiBr_2 , NiI_2 , NiCl_2 , CuF_2 , CuBr_2 ,
4 CuI_2 , CuF_2 , CuI , CuCl , CuBr , VF_5 , VF_4 , VF_3 , VF_2 , VCI_4 , VCl_3 ,
5 VBr_4 , VBr_3 , VI_3 , CrF_2 , CrF_3 , CrF_4 , CrF_5 , CrF_6 , CrCl_3 ,
6 CrCl_4 , CrBr_3 , CrBr_4 , CrI_3 , MnCl_2 , MnCl_3 , MnCl_4 , MnBr_3 ,
7 MnI_3 , ScCl_3 , ScBr_3 , ScF_3 , TiCl_4 , TiBr_4 , TiF_4 , MoCl_3 ,
8 $\text{Mo}_2\text{Cl}_{10}$, MoBr_4 , Mo_2F_9 , MoF_6 , MoF_5 , RuF_5 , RuF_3 , RuF_4 ,
9 RuF_6 , RuCl_3 , RuCl_4 , RuCl_6 , RuBr_6 , RhF_3 , RhF_4 , RhF_6 ,
10 PdF_2 , PdCl_2 , PdBr_2 , PdI_2 , WCl_6 , WBr_5 , WCl_3 , WBr_3 , WI_3 ,
11 copper acetate, copper naphthoate, copper benzoate,
12 copper propanoate, iron acetate, iron benzoate, iron
13 naphthoate, copper 4-ethyl benzoate, iron 4-butyl benzo-
14 ate, nickel acetate, nickel benzoate, nickel naphthoate,
15 copper decanoate, iron hexanoate, iron phthalocyanine,
16 manganese phthalocyanine, copper phthalocyanine, nickel
17 phthalocyanine, iron 2-(methoxymethyl) acetate, mangan-
18 ese 3-(ethoxy) propanoate, copper 4-(propoxy carbonyl)
19 butanoate, cobalt 3-(propyl carbonyl oxy) propanoate,
20 vanadium 2-(methyl carbonyloxy methyl) acetate, copper
21 4-(ethoxy carbonyl methyl) butanoate, copper 4-(ethoxy
22 methyl) benzoate, nickel 3-(propoxy) naphthoate, cobalt
23 4-(ethoxy carbonyl) benzoate, iron 2-(hydroxy) acetate,
24 copper 2-chloro propanoate, vanadium 4-(bromo) benzoate
25 chromium 4-(hydroxy) benzoate, iron phenolate, copper
26 naphtholate, nickel 4-chloro phenolate, vanadium 5-
27 (hydroxy) naphtholate, $\text{Fe}(\text{CN})_2$, $\text{Cu}(\text{SeCN})_2$, $\text{Ni}(\text{TeCN})_2$,
28 $\text{Cr}(\text{OCN})_3$, $\text{Fe}(\text{CH}_3\text{S})_3$, $\text{Cu}(\text{CH}_3\text{CH}_2\text{S})_2$, $\text{Cc}(\text{HS})_2$,
29 $\text{Ni}(\text{CH}_3\text{CH}_2\text{CH}_2\text{Se})_2$, $\text{V}(\text{HSe})_3$, $\text{Mn}(\text{HTe})_3$, $\text{Ti}(\text{CH}_3\text{Te})_4$, and
30 mixtures thereof.

31 The preferred co-catalyst I salts include
32 copper:bromide, chloride, iodide and acetate; iron:
33 bromide, chloride, iodide, and acetate; manganese:
34 iodide, chloride, bromide, and acetate and mixtures
35 thereof.

36 Co-catalyst II is the term used herein to des-
37 ccribe at least one organic or inorganic salt included
38 within the classes of alkali and alkaline earth metal:

1 halides, hydroxides, carboxylates, aryloates, aryolates,
2 pseudo halides; tetra hydrocarbyl phosphonium: halides,
3 hydroxides, carboxylates, aryloates, aryolates and
4 pseudo halides; and tetra hydrocarbyl ammonium: halides,
5 hydroxides, carboxylates, aryloates, aryolates, pseudo
6 halides ; and miscellaneous salts described hereinafter.

7 More specifically, the co-catalyst II salt
8 preferably comprises at least one cation and an anion,
9 said cation being independently selected from the group
10 consisting of alkali metal cations including those of Li,
11 Na, K, Rb, Cs, Fr; alkaline earth metal cations including
12 those of Be, Mg, Ca, Sr, Ba, and Ra; and tetra hydrocar-
13 byl phosphonium and ammonium cations represented by the
14 respective structural formulae: $(R_6)_4P^+$ and $(R_6)_4N^+$
15 wherein each R_6 is a hydrocarbyl group independently
16 selected from the group consisting of substituted and
17 unsubstituted: alkyl, typically alkyl having from about
18 1 to about 30 carbons, preferably from about 1 to about
19 20 carbons, and most preferably from about 1 to about
20 10 (e.g., 1-5) carbons, aryl, preferably aryl having from
21 6 to about 14 carbons, and most preferably from 6 to
22 about 10 carbons, and alkaryl and aralkyl wherein the
23 aryl and alkyl groups thereof are as described immediate-
24 ly above; said R_6 substituents being as defined in connec-
25 tion with the substituents of R_1 described above. Ac-
26 cordingly, the term hydrocarbyl is intended to include
27 both substituted and unsubstituted groups, and mixtures
28 thereof.

29 The anion of co-catalyst II includes any of the
30 anions described in conjunction with co-catalyst I, in-
31 cluding halides, hydroxylate, carboxylate, aryloate,
32 aryolate, pseudo halide, and "miscellaneous anions"
33 defined herein to be selected from the group consisting of
34 R_5S^- , HS^- , R_5Se^- , HSe^- , HTe^- , and R_5Te^- , R_5 being as
35 described above.

36 More specifically, representative co-catalyst II
37 alkali and alkaline earth metal halides include the Li,

1 Na, K, Rb, and Cs, iodides, bromides, chlorides, and
2 fluorides; and the Mg, Ca, Sr, and Ba, iodides, bromides,
3 chlorides, and fluorides and mixtures thereof. Preferred
4 co-catalysts II of this class include the Na, K, Rb, Cs,
5 Mg, and Ca halides.

6 Suitable co-catalysts II alkali and alkaline
7 earth metal hydroxides include LiOH, NaOH, KOH, RbOH,
8 CsOH, Ca(OH)₂, Ba(OH)₂, Mg(OH)₂ and mixtures thereof.

9 Preferred co-catalysts II of this class include
10 the Na, K, Rb, Mg, and Ca hydroxides.

11 Representative co-catalyst II alkali and alka-
12 line earth metal: carboxylates, aryloates, and aryolates
13 include sodium acetate, potassium acetate, calcium ace-
14 tate, cesium acetate, magnesium acetate, potassium ethan-
15 oate, sodium propanoate, magnesium butanoate, strontium
16 pentanoate, sodium benzoate, potassium benzoate, magnes-
17 ium benzoate, calcium benzoate, sodium naphthoate,
18 potassium naphthoate, beryllium naphthoate, sodium 4-
19 (6-methyl-2-naphthyl) pentanoate, potassium 3- (7-methyl-
20 1-naphthyl)-propanoate, magnesium 2- (4-propyl-1-benzyl)
21 ethanoate, calcium phenolate, sodium naphtholate, potas-
22 sium naphtholate, sodium 3- (ethoxy) propanoate, potas-
23 sium 4- (propoxy carbonyl) butanoate, calcium 3- (propyl
24 carbonyl oxy) propanoate, magnesium 2-(methyl carbonyl
25 oxy methyl) acetate, beryllium 4- (ethoxy carbonyl methyl)
26 butanoate, cesium 4- (ethoxy methyl) benzoate, sodium 3-
27 (propoxy) naphthoate, potassium 4- (ethoxy carbonyl)
28 benzoate, barium 2- (hydroxy) acetate, rubidium 2-
29 chloropropanoate, magnesium 4-bromobenzoate, magnesium
30 phenolate, and mixtures thereof.

31 Preferred co-catalysts II of this class include
32 the K, Rb, and Cs acetates.

33 Representative examples of co-catalyst II alkali
34 and alkaline earth pseudo halides include NaSCN, KCN,
35 NaSeCN, KSeCN, CsSeCN, NaTeCN, KTeCN, NaOCN, NaCNO, KOON,
36 KCNO, CsOCN, CsCNO, CsTeCN, Mg(SeCN)₂, Mg(TeCN)₂, Mg(OCN)₂
37 Mg (CNO)₂, Ca(SeCN)₂, Ca(TeCN)₂, Ca(OCN)₂, and Ca(CNO)₂

1 and preferably the Na, K, Rb, and Cs thiocyanates.

2 Representative examples of suitable co-catalyst
3 II tetra hydrocarbyl ammonium and phosphonium halide,
4 pseudo halide, hydroxide, carboxylate, aryloate, aryolate
5 salts include tetra methyl ammonium bromide, tetra ethyl
6 phosphonium chloride, tetra decyl phosphonium bromide,
7 tetra phenyl ammonium chloride, tetra phenyl phosphonium
8 bromide, dimethyl diethyl ammonium iodide, methyl trie-
9 thyl phosphonium chloride, tetra butyl ammonium chloride,
10 phenyl trimethyl ammonium bromide, phenyl trimethyl phos-
11 phonium chloride, phenyl triethyl ammonium iodide, phenyl
12 triethyl phosphonium chloride, tetra ethyl ammonium
13 hydroxide, tetra butyl ammonium hydroxide, tetra ethyl
14 phosphonium hydroxide, phenyl triethyl ammonium hydroxide,
15 phenyl trimethyl phosphonium hydroxide, tetraethyl ammon-
16 ium acetate, tetra butyl phosphonium acetate, phenyl
17 triethyl ammonium acetate, phenyl trimethyl phosphonium
18 acetate, tetraethyl ammonium benzoate, phenyl trimethyl
19 phosphonium benzoate, phenyl triethyl ammonium naphtho-
20 ate, tetra ethyl ammonium phenolate, tetra butyl phosphon-
21 ium naphtholate, tetra 2-(methoxy) ethyl phosphonium
22 chloride, tetra 4-(propoxy methyl) phenyl ammonium bro-
23 mide, di 3- (methoxy carbonyl) -propyl -diethyl phosphon-
24 ium iodide, di 4- (ethyl carbonyloxy) butyl-dimethyl
25 ammonium chloride, tetra 5-(ethoxy carbonyl methyl)
26 pentyl phosphonium bromide, tetra 4-hydroxy butyl ammon-
27 ium acetate, tetra 3-chloropropyl phosphonium acetate,
28 tetra methyl ammonium thiocyanate, tetra ethyl phosphon-
29 ium seleno cyanate, tetra (4-methyl phenyl) ammonium
30 chloride, tetra (3-phenyl-1-propyl) phosphonium bromide.

31 Preferred co-catalysts II of this class include
32 the unsubstituted tetra lower alkyl (e.g., C₁ to C₅
33 alkyl) ammonium or phosphonium hydroxides, iodides, bro-
34 mides, fluorides, chlorides and acetates.

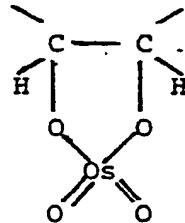
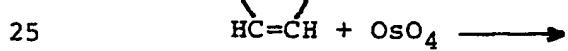
35 Representative co-catalyst II alkali, alkaline
36 earth metal salts possessing the miscellaneous group of
37 anions described above include Na(CH₃S), K(CH₃-CH₂-S),

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1 RbHS, CsHSe, Ca(HTe)₂, Ba(CH₃Te)₂, and mixtures
 2 thereof.

3 Representative co-catalyst II tetra hydrocarbyl
 4 ammonium and phosphonium salts possessing the miscella-
 5 neous groups of anions include (CH₃-CH₂)₄PHSe,
 6 (CH₃)₄NHS, (C₆H₆)₄PHTe, (CH₃)₄PCH₃S, (CH₃-CH₂)₄N CH₃-
 7 CH₂Se, (C₆H₆)₄PCH₃S, (CH₃-CH₂)₄NHSe and mixtures thereof.

8 The aforescribed catalyst composition comprising
 9 at least the two components of catalytically active metal
 10 oxide and co-catalyst I, and optionally the third component
 11 of co-catalyst II, unexpectedly generally improves selec-
 12 tivity of reactions for hydroxylating olefins with
 13 molecular oxygen up to about 100%. Although the exact
 14 mechanism and reason for this effect is not fully under-
 15 stood, it is considered that the results speak positively
 16 for themselves. However, the following is offered as an
 17 explanation of the mechanism for the observed catalytic
 18 effect in connection with the use of osmium tetroxide
 19 as the catalytically active metal oxide, although such
 20 explanation is not intended to be exhaustive of all pos-
 21 sible mechanistic details. It is known that osmium te-
 22 troxide adds across the olefinic double bond of the com-
 23 pound to be hydroxylated to yield an intermediate cis-
 24 ester as follows:



30 The osmium complex is now formally in the +6
 31 oxidation state. The glycol product can be obtained
 32 from this complex by a reductive procedure which is com-
 33 monly used in the well-known stoichiometric procedure
 34 wherein the osmium compound acts as the oxidant or it can
 35 be obtained by oxidative hydrolysis which is believed to
 36 be operating in the present invention.

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1 Considering this system, it is believed that the
2 anion of co-catalysts I and/or II acts to facilitate the
3 hydrolysis of the glycolate while the transition metal of
4 co-catalyst I mediates the oxidation of the osmium by
5 molecular oxygen. The reoxidation is also believed to be
6 facilitated by the pH and temperature of the reaction
7 medium.

8 Similar mechanisms are believed to be operating
9 in connection with the other catalytically active metal
10 oxides described herein.

11 Thus, while the presence of co-catalyst I is es-
12 sential to achieving improvements in selec-
13 tivity and/or yield of the hydroxylation reaction a still
14 further improvement in these results may be obtained by
15 the additional presence of co-catalyst II.

16 Accordingly, in view of the above explanation,
17 it is recommended that the most pre-
18 ferred valence of the transition metals of co-catalyst
19 I as initially employed be that which represents the high-
20 est stable oxidation state thereof, since such metals
21 must be capable of being reduced upon oxidizing the Os⁺⁶.
22 While this is not critical, it avoids the need in some
23 instances to oxidize the transition metal in-situ so that
24 it can be reduced.

25 It is also critical to have water present dur-
26 ing the hydroxylation reaction since the water not only
27 serves to hydrolyze the cis-ester intermediate but it
28 is also believed to contribute one of the oxygen mole-
29 cules constituting one of the hydroxyl groups in the
30 resulting glycol. The source of this water, however,
31 may vary. Thus, the water formed in-situ during the
32 reaction can contribute to the water for
33 the reaction. However, if more is needed it can be
34 added separately.

35 In the practice of the present invention, the
36 hydroxylation reaction is carried out in the presence
37 of catalytic amounts of the catalytically active metal

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1 oxide, co-catalyst I and optional co-catalyst II.
2 While any amount of each component in the two or three
3 component catalyst system effective to catalyze the
4 reaction is sufficient, it is preferred that such effec-
5 tive amounts constitute typically from about 10^{-5} to
6 about 10^{-2} moles, preferably from about 5×10^{-5} to
7 about 5×10^{-2} moles, and most preferably from about
8 10^{-4} to about 10^{-3} moles of the catalytically active
9 metal oxide per mole of ethylenic unsaturation to be
10 hydroxylated in the olefin; typically from about 1 to
11 about 1,000 mole percent, preferably from about 100 to
12 about 500 mole percent, and most preferably from about
13 200 to about 30 mole percent, co-catalyst I based on the
14 total number of moles of metal in the catalytically ac-
15 tive metal oxide employed; and typically from about 0 to
16 about 500 mole percent, preferably from about 50 to
17 about 300 mole percent, and most preferably from about
18 100 to about 150 mole percent, co-catalyst II, based on
19 the total number of moles of the metal in the catalytic-
20 ally active metal oxide.

21 Preferably where OsO_4 is employed as the
22 catalytically active metal oxide, such catalytically
23 effective amounts may be e.g. from 10^{-5} to 5×10^{-1} moles,
24 preferably 10^{-5} to 10^{-1} moles, more preferably from about 10^{-4}
25 to about 10^{-3} moles OsO_4 per mole of ethylenic unsatura-
26 tion to be hydroxylated in the olefin; typically from
27 about 1 to about 1,000 mole percent, preferably from
28 about 100 to about 500 mole percent, co-catalyst I, based
29 on the total number of moles osmium in the OsO_4 ; and
30 typically from about 0 to about 500 mole percent, prefer-
31 ably from about 100 to about 150 mole percent, co-
32 catalyst II, based on the total number of moles of osmium
33 in the OsO_4 .

34 Also included in the term osmium tetroxide as
35 used herein are osmium compounds which are converted to
36 osmium tetroxide during the course of reaction such as
37 salts thereof including K, Na, and Li osmates and the

1 like.

2 While the hydroxylation reaction can be con-
3 ducted in a heterogeneous system, the preferred mode for
4 conducting the hydroxylation reaction is in a liquid
5 reaction mixture, preferably provided as a homogeneous
6 or substantially homogeneous medium by using an inert
7 organic solvent to dissolve, where possible, whatever
8 components are employed in the catalyst system and reac-
9 tants. The solvent is entirely optional, however, and
10 when present functions primarily to achieve even disper-
11 sal of heat in the reaction mixture. Partial immiscibil-
12 ity of the solvent with water is acceptable although not
13 preferred. By an inert solvent is meant one which does
14 not undergo oxidation during the course of the reaction.

15 Suitable inert organic solvents include ali-
16 phatic or aromatic alcohols having from 1 to about 10
17 carbon atoms, preferably tertiary alcohols, aliphatic or
18 aromatic ketones having from 3 to about 10 carbon atoms,
19 aliphatic or alicyclic ethers having from 2 to about 10
20 carbon atoms, glycols having from 2 to about 10 carbon
21 atoms, N, N-dialkyl amides having from 3 to about 10
22 carbon atoms, nitriles having from about 2 to about 10
23 carbons, aliphatic or aromatic sulfoxides having from 2
24 to about 14 carbon atoms, aliphatic or aromatic sulfones
25 having from 2 to about 14 carbon atoms, and the like.

26 Examples of suitable solvents include methanol, ethanol,
27 propanol, butanol, hexanol, decanol, t-butyl alcohol,
28 t-amyl alcohol, benzyl alcohol, acetone, methylethyl
29 ketone, methylbutyl ketone, acetophenone, ethylene
30 glycol, propylene glycol, diethylene glycol, tetra-
31 ethylene glycol, dimethyl formamide, diethyl formamide,
32 dimethyl acetamide, dimethyl sulfoxide, diethyl sulfox-
33 ide, di-n-butyl sulfoxide, diphenyl sulfoxide, dibenzyl
34 sulfoxide, dimethyl sulfone, diethyl sulfone, tetra-
35 methylene sulfone, diphenyl sulfone, acetonitrile,
36 pyridine, dioxane, tetrahydrofuran, tetrahydropyran,
37 dioxolane, and mixtures thereof.

1 The preferred solvents include those which are
2 substantially or completely miscible with water such as
3 t-butyl alcohol, methanol, and acetonitrile, as well as
4 glycols and/or polyols derived from the olefin being
5 hydroxylated.

6 The inert solvent is preferably employed in
7 amounts sufficient to achieve a homogeneous solution with
8 respect to at least the olefin and catalyst system.
9 Typically such amounts can vary from about 0 to about 90%
10 (e.g., 10 to 90%), preferably from about 20 to about 80%,
11 and most preferably from about 20 to about 50%, by
12 weight, based on the total weight of the reaction mixture.

13 Water is provided to, and/or is present in, the
14 initial reaction mixture in at least a stoichiometric
15 molar ratio with the molar amount of ethylenic unsatura-
16 tion to be hydroxylated in the olefin. Such ratios
17 preferably are also present in the reaction mixture at
18 any given time after start-up. Accordingly, water is
19 present in the reaction mixture at molar ratios, of
20 water to ethylenic unsaturation to be hydroxylated in
21 the olefin of from about 1:1 to about 100:1, preferably
22 from about 1:1 to about 10:1, and most preferably from
23 about 1:1 to about 2:1. Such molar ratios typically
24 can be achieved by controlling the amount of water in
25 the reaction mixture to be from about 2 to about 90%,
26 preferably from about 15 to about 85%, and most prefer-
27 ably from about 20 to about 60%, by weight, based on
28 the total weight of the reaction mixture. Preferably
29 the amount of water employed is less than that which
30 will cause separation of the reaction mixture into an
31 aqueous phase and organic phase.

32 The pH of the reaction mixture during the hy-
33 droxylation reaction preferably should not be allowed
34 to drop below about 4 otherwise the selectivity of the
35 reaction drops drastically. Likewise, if the pH of the
36 reaction exceeds about 10, over oxidation of the olefin
37 may occur to an increasingly greater degree as the pH

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1 approaches 14. Accordingly, the pH of the reaction mix-
2 ture typically is maintained between about 4 and 10,
3 preferably between about 5 and about 9, and most prefer-
4 ably between about 6 and about 9 (e.g., 6 to 8). It is
5 an advantage of the present invention that the pH of the
6 reaction mixture using the ingredients described herein
7 naturally falls within the range of about 6 to about 8
8 and consequently does not have to be controlled thereby
9 simplifying the process. However, if the pH of the reac-
10 tion mixture should drift for some reason within the un-
11 desirable ranges, conventional buffers or bases may be
12 employed to limit such drift.

13 The primary oxidant employed in the present in-
14 vention is molecular oxygen. Such oxygen can be added
15 as a pure oxygen or as part of an oxygen containing gas
16 such as air or some other oxygen containing gas having
17 one or more inert components such as CO₂ or N₂ present
18 therein. Generally, the oxygen containing gas is present
19 within, preferably dissolved in, the reaction mixture
20 in amounts sufficient to achieve hydroxylation of the
21 olefin.

22 Accordingly, the molar ratio of oxygen to olefin
23 ethylenic unsaturation can vary widely but for safety
24 reasons it is preferably maintained outside explosive
25 limits.

26 For example, when hydroxylating ethylene or pro-
27 pylene, if oxygen is in excess of stoichiometry, the ratio
28 typically will be 98 weight % oxygen or more and 2% or
29 less of the olefin. Preferably, however, the olefin is
30 employed in excess, preferably large excess, of stoichio-
31 metry, and the oxygen concentration of the oxidizing gas
32 typically will be about 10 weight % oxygen and about 90
33 weight % olefin. When oxygen is in excess of stoichiometry,
34 olefin can be added during the reaction. On the
35 other hand, where the olefin is in excess of stoichiometry,
36 oxygen can be added during the reaction as the oxygen is

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1 consumed.

2 Accordingly, in view of the above, the oxygen
3 containing gas preferably is dissolved in the reaction
4 mixture in an amount sufficient to achieve a molar ratio
5 of ethylenic unsaturation to be hydroxylated in the
6 olefin to oxygen in excess of 1:1 typically up to as
7 high as 100:1; and outside the explosive limits of the
8 reaction mixture. It is to be noted, however, then when
9 either olefin or O_2 is employed in substantial excess of
10 stoichiometry for safety reasons the conversion in a
11 batch process will necessarily be very low. This is not
12 a problem in a continuous process since unreacted com-
13 ponents are recycled.

14 The hydroxylation reaction is typically con-
15 ducted at temperatures of from about 40 to about 150°C,
16 preferably from about 60 to about 120°C, and most
17 preferably from about 80 to about 100°C, to achieve high
18 selectivities for the hydroxylated olefin.

19 At temperatures greater than the aforesaid
20 ranges, the reaction rate increases substantially but
21 this usually occurs at the expense of a significant re-
22 duction in selectivity. At very low reaction tempera-
23 tures, e.g., below about 0°C, the reaction rate decreases
24 to a commercially undesirable degree. Accordingly,
25 while the reaction temperature is not critical and can
26 vary over a wide range, one normally would not operate
27 at temperature extremes outside the aforesaid ranges.

28 For the production of ethylene glycol, propy-
29 lene glycol or any glycol derived from any unsaturated
30 gaseous olefin, the latter may be bubbled through the
31 reaction mixture containing the components described
32 herein or it may be introduced under pressure. Like-
33 wise with the oxygen containing gas. However, it is
34 preferred that the reaction takes place in the liquid
35 phase. Consequently, sufficient pressure is preferably
36 employed to maintain the gaseous reactants (i.e., olefin
37 and oxygen) in the liquid phase.

1 Although the magnitude of the pressure is not
2 critical, it determines the amount of the gaseous reac-
3 tants that are present in the reaction mixture and there-
4 fore affects the rate of reaction. Accordingly, the
5 total pressure of the gases in contact with the reac-
6 tion mixture is typically controlled to be from about
7 200 to about 2,000 psig, preferably from about 300 to
8 about 1500 psig, and most preferably from about 100 to
9 about 1,000 psig at the aforesaid reaction temperatures.
10 The partial pressure of each reactant gas, i.e., olefin
11 and oxygen, can be controlled to achieve the aforesaid
12 molar ratios. When the reactant olefin gas is ethylene,
13 the partial pressure (at reaction temperatures) thereof
14 is typically controlled to be from about 100 to about
15 2,000 psig, preferably from about 200 to about 1,500
16 psig, and most preferably from about 400 to about 1,000
17 psig; while when propylene is the reactant olefin, the
18 partial pressure (at reaction temperatures) thereof is
19 typically controlled to be from about 100 to about 2,000
20 psig, preferably from about 400 to about 1,500 psig and
21 most preferably from about 400 to about 1,000 psig to
22 provide a suitable reaction rate.

23 When the olefin reactant is a liquid or is
24 dissolved in the reaction mixture under pressure, its
25 concentration in the reaction mixture typically will
26 vary from about 1 to about 90%, preferably from
27 about 20 to about 80%, and most preferably from about
28 60 to about 80%, by weight, based on the total weight of
29 the reactant mixture.

30 The hydroxylation reaction can be performed as
31 a batch reaction, as a continuous reaction or as a semi-
32 continuous reaction. In the batch reaction, the cataly-
33 tically active metal oxide, e.g., OsO_4 , is charged into
34 the reaction vessel as a solution in the inert solvent
35 along with the co-catalyst I and optional co-catalyst II,
36 water, and olefin if in liquid form. The reaction vessel
37 is then pressurized with oxygen and olefin if in gaseous

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1 form. It may be desirable to heat the liquid reaction
2 mixture to reaction temperature prior to pressurizing
3 with the reactant gases. The reaction is allowed to pro-
4 ceed to completion.

5 In the continuous process, the components can
6 be introduced into the inlet of an elongated reactor at
7 a rate such that substantially complete reaction will
8 have taken place by the time the reaction mixture reaches
9 the reactor outlet. The reaction can be carried out in
10 a semi-continuous manner by metering the reactant mix-
11 ture components into a series of two or more tank reac-
12 tors at the appropriate rate to maintain the reactor
13 liquid level.

14 The spent reaction mixture after removal of un-
15 reacted olefin is a solution of product glycol, by-
16 products if any, solvent, water, and catalyst system
17 components. The volatile components are distilled out
18 of the reaction mixture into various fractions leaving
19 non-volatile catalyst system components in the still.
20 The product glycol is then separated from the high boil-
21 ing distillate.

22 The following examples are given as specific
23 illustrations of the claimed invention. It should be
24 understood, however, that the invention is not limited
25 to the specific details set forth in the examples. All
26 parts and percentages in the examples as well as in the
27 remainder of the specification are by weight unless
28 otherwise specified.

29 In the following examples, selectivity, yield,
30 and conversion are calculated as follows:

31 % Selectivity = Moles of glycol x100
32 Moles of Oxygenated
33 Product
34 % Conversion = Moles of product x100
35 Moles of Olefin
36 Charged
37 % Yield = (% conversion x % selectivity)
 ÷ 100

1 Furthermore, all analysis of reaction products
2 is conducted by gas chromatography.

3 EXAMPLE 1

4 Into a 300 ml titanium autoclave is charged
5 0.05g of osmium tetroxide as a 0.5% solution thereof in
6 t-butanol, 0.67 of Cu Cl₂ (co-catalyst I), 0.5g tetra-
7 ethyl ammonium bromide (co-catalyst II), 10.9g of ace-
8 tonitrile, and 76.6g of water. Propylene (36.7g) is
9 added to the autoclave under a pressure of 140 psig, and
10 the reaction mixture warmed to 100°C. Oxygen is added
11 slowly (over a period of 20 min.) until a pressure increase in the
12 autoclave of 103 psig is obtained. The mixture is stirred for 140
13 minutes starting from the time of O₂ addition and then
14 cooled to 25°C. The molar ratio of propylene to O₂
15 metered into the reaction mixture is about 20:1. The pH
16 of the reaction mixture during the course of the reaction
17 ranges from 5 to 7. The product solution is analyzed by
18 gas chromatography and indicates the production of 3.14g of
19 propylene glycol which is a yield of 5%, a selec-
20 tivity of 99%, and a conversion of 5%, based on the
21 propylene charged. No other detectable products such as
22 ketones or polyols are generated under these conditions.

23 EXAMPLE 2

24 Into a 300 ml titanium autoclave is charged
25 at room temperature (25°C) 46.4g propylene at a pressure
26 of 160 psig, 0.05g of osmium tetroxide (0.5% t-butanol
27 solution), 1.03g sodium bromide (co-catalyst II) 66.2g
28 water, and 0.6g of Cu Cl₂ (co-catalyst I). After warm-
29 ing the mixture to 100°C, to this solution is slowly
30 added over a period of 10 minutes, oxygen until a pres-
31 sure increase of 127 psig is obtained. The molar ratio
32 of propylene to O₂ metered into the reaction mix-
33 ture is about 20:1. (Note the slow addition of O₂ is to
34 maintain its concentration outside explosive limits.)
35 The reaction mixture is stirred at 100°C for 2.5 hours
36 upon completion of O₂ addition and then cooled to room
37 temperature. The pH of the reaction mixture is 6.0.

1 Propylene glycol (2.96g) is produced in an amount which
2 corresponds to a selectivity greater than 99%. The con-
3 version of the reaction is 4%.

4 EXAMPLE 3

5 Into a 300 ml titanium autoclave is charged
6 0.2 mmole osmium tetroxide (0.5% t-butanol solution),
7 1.10g Cu Br₂ (co-catalyst I), 2.02g of tetraethyl am-
8 monium bromide (co-catalyst II), 79.9g of H₂O, 6.7g of
9 acetonitrile and 36.5g propylene at a pressure of 170
10 psig (25°C). The reaction mixture is then warmed to
11 100°C. To this solution is slowly added over a period
12 of 15 minutes O₂ until a pressure increase of 127 psig
13 is obtained. The molar ratio of propylene to O₂ metered
14 into the reaction mixture is about 20:1. The solution is
15 stirred at 100°C for 2 hours upon completion of O₂ addition
16 and then cooled to room temperature. The pH of the reac-
17 tion mixture during the reaction is about 5. Propylene
18 glycol (3.32g) is produced in an amount indicating
19 in excess of 99% selectivity. The conversion is 4.4%.

20 EXAMPLE 4

21 The procedure of Example 1 is followed except
22 that the materials added to the reaction autoclave are
23 as follows: 0.05g OsO₄ (0.5% t-butanol), CuCl₂ 0.4g,
24 NaCl 0.1g, H₂O 43.4g, methanol 19.9g. The reaction mix-
25 ture is warmed to 80°C and 21.9g of propylene (400 psig)
26 is then added. Air is then introduced to the autoclave
27 at 300 psig over a period of about 5 minutes. Olefin to
28 O₂ ratio 60:1. The reaction mixture is then stirred
29 for 2 hours upon completion of air addition. The pH of
30 the reaction mixture during the reaction is about 5.
31 The selectivity for propylene glycol is greater than 99%
32 and the conversion is about 2%.

33 EXAMPLE 5

34 To a 300 ml titanium autoclave is charged
35 0.05g (0.2 mmole) OsO₄, 0.66g CuCl₂, 0.58g NaCl, 11.7g
36 t-butanol, 58.0g of water and ethylene to a pressure of
37 400 psig (25°C) and the resulting mixture is warmed to
38 100°C.

1 Oxygen is added slowly over a period of 10 minutes until
2 a pressure increase of 100 psig is obtained. The pH
3 of the reaction mixture is about 5.5. The reaction mix-
4 ture is stirred at 100°C for 2.5 hours upon completion
5 of O₂ addition and the products analyzed. Ethylene
6 glycol (1.35g, 21.8 mmole) is produced at 70% selectiv-
7 ity and 10% yield.

8 EXAMPLE 6

9 The following example illustrates the effect
10 of omitting co-catalyst II from the reaction mixture.

11 Following the procedures of Example 5 to a
12 300 ml titanium autoclave is charged 0.05g (0.2 mmole)
13 OsO₄, 1.32g CuCl₂, 18.8g t-butanol, and 57.0g H₂O.
14 Ethylene is charged under a pressure of 400 psig (25°C)
15 and the reaction mixture is warmed to 100°C. Oxygen is
16 added slowly over a period of about 5 minutes until a
17 pressure increase of 100 psig is obtained. (Molar
18 ratio of olefin: O₂ is about 20:1.) The reaction mix-
19 ture (pH about 5) is stirred for 2.5 hours upon comple-
20 tion of O₂ addition at a temperature of 100°C. The
21 product analysis (gas chromatography) indicates 0.72g
22 (11.0 mmole) ethylene glycol is produced at a selectiv-
23 ity of 39.2%, and 5% yield.

24 The following comparative examples are in-
25 tended to illustrate the effect on glycol selectivity
26 and yield when one omits co-catalyst I from the reac-
27 tion components of the tri-component catalyst system.

28 Comparative Example 1

29 The procedure of Example 2 is followed ex-
30 cept that the materials added to the reaction autoclave
31 are as follows: propylene 32.8g at 160 psig (25°C),
32 OsO₄ 0.05g (0.20 mmole) as 0.5% solution in t-butanol,
33 tetraethylammonium bromide 1.06g (5.0 mmoles), H₂O
34 75.8g, acetonitrile 8.1g. Oxygen is added until a
35 pressure of 100 psig is obtained (olefin to O₂ molar
36 ratio 20:1); with stirring at 100°C for 2.5 hours upon
37 completion of O₂ addition. The pH of the reaction

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1 mixture during reaction is about 5. In the absence of
2 co-catalyst I, substantially no propylene glycol is
3 formed, i.e., selectivity is about 0%, and con-
4 version is about 0%.

5 Comparative Example 2

6 The following comparative example illustrates
7 the affect of omitting OsO_4 from the reaction mixture.
8 The procedure of Example 2 is followed except that the
9 materials added to the reaction autoclave are as follows:
10 propylene 49.7g (at 160 psig and 25°C), CuBr_2 1.10g,
11 tetraethylammonium bromide 1.05g, H_2O 80g, and aceton-
12 trile 7.5g. The reaction mixture is warmed to 100°C. Oxy-
13 gen is then added until a pressure increase of about
14 100 psig is obtained (olefin to O_2 molar ratio 20:1).
15 The resulting reaction mixture is stirred at 100°C for
16 2.5 hours upon completion of O_2 addition. The pH of
17 the reaction mixture during the reaction is about 5.
18 Propylene glycol is formed in amount of about 0.30g
19 (4.0 mmoles), i.e., in the absence of the catalytically ac-
20 tive metal oxide substantially no propylene glycol is
21 formed.

22 As may be seen from a comparison of Example 5
23 with Example 6, the omission of co-catalyst II in
24 Example 6 results in a reduction of selectivity.

25 The principles, preferred embodiments, and
26 modes of operation of the present invention have been
27 described in the foregoing specification. The invention
28 which is intended to be protected herein, however, is
29 not to be construed as limited to the particular forms
30 disclosed, since these are to be regarded as illustra-
31 tive rather than restrictive. Variations and changes may
32 be made by those skilled in the art without departing
33 from the spirit of the invention.

CLAIMS

1. A process for hydroxylating at least one olefinic compound having at least one ethylenic unsaturation which comprises reacting said olefinic compound with oxygen and water in the presence of a catalyst composition in a manner and under conditions sufficient to convert at least one of said ethylenic unsaturation to its corresponding diol, said catalyst composition comprising:

- (a) at least one catalytically active metal oxide wherein the metal of said oxide is selected from the group consisting of Os, Ti, Zr, Nb, Cr, Mo, W, Ru, Re, and Ir; and
- (b) at least one co-catalyst I transition metal salt having a cation and an anion wherein said cation is of a transition metal independently selected from the group consisting of Fe, Co, Ni, Cu, V, Cr, Mn, Sc, Ti, Mo, Ru, Rh, Pd, and W; and said anion is of a member independently selected from the group consisting of halide, carboxylate, aryloate, aryolate, pseudo halide, R_5S^- , HS^- , R_5Se^- , HSe^- , HTe^- , and R_5Te^- , R_5 being alkyl of from 1 to 10 carbons; and
- (c) optionally at least one co-catalyst II having a cation and an anion wherein said cation is of a member independently selected from the group consisting of alkali metal, alkaline earth metal, tetra hydrocarbyl ammonium, and tetra hydrocarbyl phosphonium, said hydrocarbyl group being selected from the group consisting of substituted and unsubstituted alkyl, aryl, alkaryl, and aralkyl

and said anion is of a member independently selected from the group consisting of halide, carboxylate, aryloate, aryolate, pseudo halide, hydroxyl, R_5S^- , HS^- , R_5Se^- , HSe^- , HTE^- , and R_5Te^- , said R_5 being alkyl as defined above.

2. A process according to claim 1 wherein said catalyst composition comprises at least one co-catalyst I and at least one co-catalyst II.

3. A process according to claim 1 or 2 wherein the transition metal cation of co-catalyst I is of copper.

4. A process according to claim 1, 2 or 3 wherein the olefinic compound contains from 2 to 20 carbons, the metal of the catalytically active metal oxide is osmium; the cation of co-catalyst I is of a member independently selected from the group consisting of Cu, Fe, Ni, Co, and Mn; the anion of co-catalyst I is of a member independently selected from the group consisting of halide, carboxylate, aryloate, and aryolate; the cation of co-catalyst II is of a member selected from the group consisting of alkali metal, alkaline earth metal, tetra hydrocarbyl ammonium, and tetra hydrocarbyl phosphonium, said hydrocarbyl group being selected from the group consisting of alkyl, aryl, and mixtures thereof; and the anion of co-catalyst II, is of a member independently selected from the group consisting of halide, carboxylate, aryloate and aryolate.

5. A process according to any of the preceding claims wherein the olefinic compound is selected from at least one member of the group consisting of ethylene and propylene; the catalytically active metal oxide is OsO_4 ; the co-catalyst I salt is selected from the group consisting

of transition metal halide, transition metal acetate, transition metal benzoate and transition metal phenolate; and the co-catalyst II salt is selected from the group consisting of alkali metal halide, alkaline earth metal halide, alkali metal acetate, alkaline earth metal acetate, tetra hydrocarbyl ammonium halide wherein the hydrocarbyl group is selected from the group consisting of alkyl having from 1 to 5 carbons, and aryl having from 6 to 10 carbons, tetra hydrocarbyl phosphonium halide, tetra hydrocarbyl ammonium acetate, and tetra hydrocarbyl phosphonium acetate wherein the respective hydrocarbyl groups are as defined above.

6 A process according to claim 1 or 2 which comprises admixing to form a liquid reaction mixture:

- (1) at least one olefinic compound having at least one ethylenic unsaturation;
- (2) a catalyst composition comprising:
 - (a) at least one said catalytically active metal oxide;
 - (b) at least one said co-catalyst I transition metal salt; and
 - (c) optionally at least one said co-catalyst II;
- (3) an oxygen containing gas; and
- (4) water in at least a stoichiometric molar ratio with the molar amount of ethylenic unsaturation to be hydroxylated in the olefinic compound.

7. A process according to any one of the preceding claims which is performed in the presence of at least one inert organic solvent.

8. A process according to claim 1 wherein the olefinic compound is ethylene and/or propylene which comprises contacting said olefinic compound with a substantially homogeneous reaction mixture having a pH of from 4 to 10, said reaction mixture comprising:

- (a) at least one inert organic solvent in an amount of from 0 to 90% by weight based on the total weight of the reaction mixture;
- (b) a catalyst composition comprising:
 - (i) osmium tetroxide in an amount of from 10^{-5} to 10^{-1} moles per mole of ethylenic unsaturation in the olefinic compound to be hydroxylated in said reaction mixture;
 - (ii) at least one co-catalyst I having a cation and an anion wherein said cation is of a transition metal selected from the group consisting of Cu, Fe, Ni, Co, and Mn, and said anion is selected from the group consisting of halide, acetate, and benzoate, said co-catalyst I being dissolved in said reaction mixture in an amount of from 1 to 1,000 mole %, based on the total number of moles of osmium metal present in said reaction mixture and
 - (iii) at least one co-catalyst II selected from the group consisting of alkali metal halide, alkaline earth metal halide, alkali metal acetate, alkaline earth metal acetate, tetra alkyl ammonium halide, tetra alkyl ammonium acetate wherein the alkyl group contains from 1 to 5 carbons, tetra alkyl phosphonium halide and

tetra alkyl phosphonium acetate wherein the alkyl group contains from 1 to 5 carbons, said co-catalyst II being dissolved in said reaction mixture in an amount of from 0 to 500 mole percent, based on the total number of moles of osmium metal present in said reaction mixture;

- (c) an oxygen containing gas dissolved in said reaction mixture in an amount sufficient to achieve a molar ratio of ethylenic unsaturation in the olefinic compound to be hydroxylated in said reaction mixture to oxygen in excess of 1:1; and
- (d) water in an amount sufficient to achieve a molar ratio of water to olefinic compound to be hydroxylated in said reaction mixture of from 1:1 to 100:1

9. A process according to claim 8 wherein co-catalyst II is selected from at least one member of the group consisting of sodium chloride, sodium bromide, potassium chloride, potassium bromide, tetra ethyl ammonium chloride, tetra ethyl phosphonium chloride, tetra ethyl ammonium bromide, tetra ethyl phosphonium bromide and mixtures thereof; co-catalyst I is selected from at least one member of the group consisting of CuCl_2 and CuBr_2 ; the inert solvent is selected from at least one member of the group consisting of ethylene glycol, propylene glycol, acetonitrile, t-butanol and methanol; and the pH of the reaction mixture is from 5 to 9.



EUROPEAN SEARCH REPORT

0077201
Application number

EP 82 30 5380

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Y	CHEMICAL ABSTRACTS, vol. 90, no. 9, 26th February 1979, page 478, no. 71786e, Columbus Ohio (USA); & JP - A - 78 127 406 (MITSUI TOATSU CHEMICALS, INC.) (07-11-1978) *The whole document*	1-9	C 07 C 29/50 C 07 C 29/03 C 07 C 31/20
Y	--- DE-C- 907 774 (BASF) *Claim; example 1*	1-9	
A	US-A-3 335 174 (C.J.NORTON) *Claims*	1	
A	--- US-A-3 337 635 (C.J.NORTON et al.) *Claims*	1	
A	--- EP-A-0 004 725 (I.C.I.) *Claims*	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
P, Y	--- EP-A-0 053 023 (EXXON RESEARCH) *Claims*	1-9	C 07 C 29/00
D, A	--- CHEMICAL ABSTRACTS, vol. 92, no. 15, April 1980, page 649, no. 128395z, Columbus Ohio (USA); & JP - A - 79 145 604 (MITSUBISHI CHEMICAL INDUSTRIES CO., LTD.) (14-11-1979) *The whole abstract*	1	
	---	-/-	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	02-03-1983	DELHOMME H.A.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
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DOCUMENTS CONSIDERED TO BE RELEVANT			Page 2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. *)
A	GB-A-1 324 763 (CONTINENTAL OIL) *Claims*	1	
A	FR-A-2 018 937 (HALCON) -----	1	
TECHNICAL FIELDS SEARCHED (Int. Cl. *)			
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 02-03-1983	Examiner DELHOMME H.A.	
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